Complex Multicompartment Micelles from Simple ABC Linear Triblock Copolymers in Solution[a]

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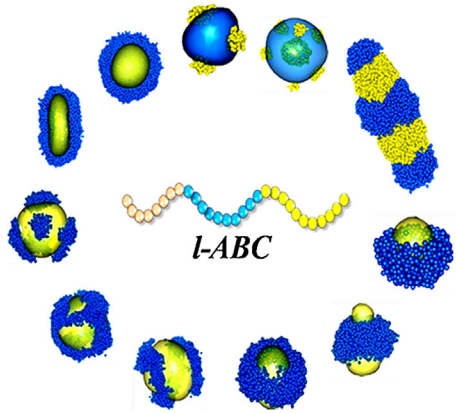
For the simple ABC linear terpolymer composed of a solvophilic A block and two solvophobic B and C blocks, the solution-state self-assembly is systematically investigated by dissipative particle dynamics (DPD) simulations, and several complex multicompartment micelles beyond the conventional wisdom, such as helix-on-sphere, cage, ring, bowl, raspberry-onion and so on, are predicted from the simulations. The detailed phase diagrams clearly point out the regions of building these complex multicompartment micelles. Thus, the complex multicompartment micelles can be obtained from the simple linear ABC terpolymers. This work advances the molecular-level understanding of multicompartment micelles from the simple linear ABC terpolymers, which will be useful for the future application of novel micelles.



1. Introduction

The self-assembly of block copolymers can provide a great variety of exquisitely ordered nanostructures,[1] which have potential applications in drug delivery,[2] microelectronic materials,[3] advanced plastics[4] and so on. In addition, several advanced synthetic methods[5–7] developed over the past decade allow us to synthesize nearly any block copolymers with the desired chemistries and architectures. Then, the following question is what block copolymers should be synthesized to satisfy the practical applications, which requires a deeper understanding of how block architecture influences structure and, thus, properties.[8] To date, the self-assembly of AB diblock copolymers with the limited micelle morphology is relatively well understood.[1] Recently, ABC triblock copolymers, which can form complex multicompartment micelles, are of fundamental interest.[9] At the beginning, for the relative ease synthesis, a plethora of linear ABC terpolymers (*l*-ABC) have been explored and the generic onion (core/shell/corona) micelle are usually obtained.[10] Therefore, more works focused on ABC miktoarm star copolymers (μ-ABC). For example, the pioneer works by Lodge and coworkers observed a variety of fascinating multicompartment micelles such as bowl micelles, worm micelles, hamburger micelles, raspberry micelles, and so on.[11–15] Moreover, a series of simulation and theoretical studies have also been performed to give a comprehensive understanding of the self-assembly of μ-ABC.[16–22] Interestingly, the recent studies on *l*-ABC by Laschewsky and co-workers reveal several complex multicompartment micelles with the fine morphology except for the proverbial

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onion morphology.[23–27] However, only a little simulation and theoretical works are paid attention to *l*-ABC.[17,20,28] It results in an absence of comprehensive understanding on the complex morphologies from *l*-ABC, especially in solutions.

Here, we report an extensive investigation of the self-assembly of *l*-ABC in solutions using dissipative particle dynamics (DPD). Marked advances of this method, allowing the exploration of the phase space to an unprecedented extent only by easily changing the relevant parameters, provide an ideal complemental means for the investigation of the micellar behavior of ABC systems and for the elucidation of fine structures.[16,17,20,28] Our simulations provide a relative comprehensive phase diagram for *l*-ABC in the dilute solutions. At the same time, a rich variety of complex multicompartment micelles with cage, worm, ring and bowl morphologies like μ-ABC are predicted. The united morphology of sphere in "sphere" and "sphere on sphere" (raspberry-onion) similar to experiments are predicted and further distinguished finely. The results complement the existing experimental and theoretical anticipation, leading to a more complete understanding of the self-assemble behavior of *l*-ABC in solutions.

2. Method and Model

DPD method is a coarse-grained particle-based dynamics simulation technique that can use larger length and time scale.[29] The details on DPD and the repulsive interactions are given in other works.[30,31] In fact, this method has been successfully applied to the self-assembly of ABC systems.[16,17,20,28] For example, Zhong and Xia[16] had defined appropriate DPD parameters and models to describe the multicompartment micelles of the famous μ-EOF miktoarm star terpolymer. Lu and coworkers[20] also used the same parameters and successfully studied the effect of chain topology on the morphological diversity of ABC terpolymers. Here, we also adopt the proved DPD parameters (listed in Figure 1) for *l*-ABC (*x*-*y*-*z*) consisted of the solvophilic block (denoted by bead A), the weakly solvophobic block (B) and the strongly solvophobic block (C), where *x*, *y*, and *z* are the number of bead A, B, and C, respectively, and denote the length of three blocks (Figure 1). Adjacent beads in a chain interact via a linear spring with the harmonic spring constant of 4. Our simulations are performed in a cubic box of size $(30r_c)^3$ containing 8.1×10^4 DPD beads, which is large enough to avoid the finite size effects. The content (volume fraction) of *l*-ABC is 0.1 to guarantee the dilute solution. For convenience, the cutoff radius, the particle mass, and the temperature are all taken as unit of the simulated system, that is, $r_c = m = k_B T = 1$. The time step Δt is taken as 0.05 and a total of $1 \approx 2 \times 10^6$ DPD time steps are carried out to guarantee the equilibration for each system.

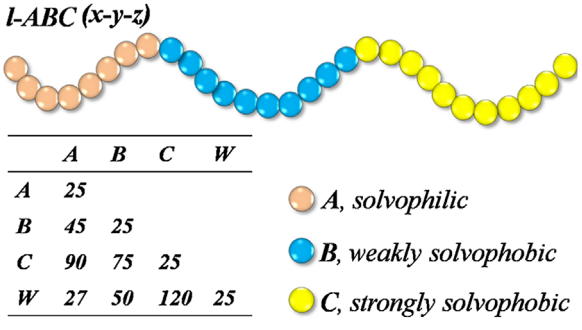

Figure 1. The coarse-grained model of the linear ABC triblock copolymer and the DPD repulsion parameters in this work.

3. Results and Discussion

By fixing the interaction parameters, we investigate the self-assemble structures of *l*-ABC terpolymers with *x*, *y*, and $z = 2$, 4, 8, and 12, respectively. Thus, we can obtain 64 *l-ABC* molecules with the different block ratios and their equilibrium micellar structures are given in Figures S1–S4. From the four figures, several general rules can be firstly obtained. The solvophilic A blocks always form the protective corona outers and the strongly solvophobic C blocks show the distinct aggregation to avoid the direct contact with the solvent, forming the humdrum spherical, elliptic, and cylindrical compartments. The most interesting is that the weakly solvophobic B blocks build the abundant morphologies, which is the key of assembling complex multicompartment micelles. Additionally, the longer solvophilic A blocks can easily result in the more discrete micelles. However, the strongly solvophobic C blocks show a reverse influence. It is that the longer solvophobic C blocks are inclined to drive the systems form the concentrative micelles. The above results are consistent with the previous studies on μ-ABC.[11,16,22,26] As shown in Figure 2, we further distinguish 18 multicompartment micelle morphologies, which are subject to five classes corresponding to Figure 2a–e, respectively. Firstly, the common onion (core/shell/corona) micelle, such as ellipse and sphere (Figure 2a1 and a2), are also validated by our simulations. Figure 3 gives the density profiles of ellipse and sphere micelle, which clearly shows the characteristic of onion morphology (Figure 3b and d) and the difference between the elliptical and spherical core (Figure 3a and c). The ellipse micelle for *l*-ABC (2-4-2) is as same as that in reference 20, which also testifies the authenticity of our simulations sidelong. Secondly, a class of interesting complex micelle morphologies is drawn in Figure 2b. The so-called raspberry-like morphology for *l*-ABC (12-12-2) (sphere on sphere, Figure 2b1) is in agreement with the

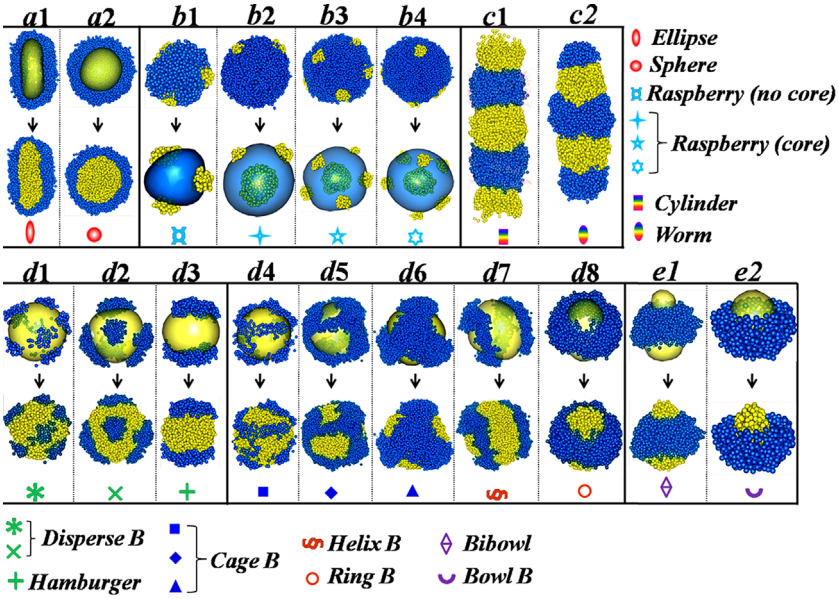

Figure 2. Complex morphologies of multicompartment micelles from simple *l*-ABC triblock copolymers in solutions (A blocks and solvents are omitted for clarity; B, blue; C, yellow).

experimental findings.[23] However, when solvophilic A blocks become a little shorter, a core of solvophobic C blocks is clearly shown in the center of raspberry micelle (Figure 2b2–b4). Here, we define the united morphologies of "sphere on sphere" (raspberry) and "sphere in sphere" (onion) as raspberry-onion-like micelle. The further experimental characterization and dynamics of the special micelle are worth giving more attention. Thirdly, the formation of cylinder and worm micelles (Figure 2c1 and c2), which are often observed in μ-ABC systems, exceeds the conventional understanding for the simple *l*-ABC systems. Fourthly, the micelles listed in Figure 2d also adopt the morphologies of core/shell/corona and the difference with the normal ones (Figure 2a) is that the shell composed of B blocks is not intact. The random discontinuous distribution of B blocks on the spherical core surface (Figure d1 and d2) let the micelles like the soccer ball, which is similar to the experimental structures.[26] The hamburger micelle with two cap-like domains (Figure d3) is also confirmed by the experiment.[26] The micelles from Figure 2d4 to 2d6 are composed of the cage of B blocks and the core of C blocks. This kind of cage structure had been found in the self-assembly of rod-coil triblock copolymers.[32,33] The morphology of micelle in Figure 2d7 is that the weakly solvophobic B blocks form the helix ribbonlike aggregate wrapping the core (helix-on-sphere). Compared with the double-helix[34,35] and helix-on-cylinder[36] superhelix multicompartment structures from different ABC terpolymer systems, it is also an interesting and novel helix micelle. The micelle in Figure 2d8 is that B blocks assemble the ring hitching the core. Finally, the experimental bowl-like micelle (Figure 2e2) for μ-ABC[12] is also found for *l*-ABC. Moreover, an interesting double-bowl-like micelle (Figure 2e1) is formed by piling up two bowl-shaped micelles by bottom to bottom. By now, we urgently disclose the complex multicompartment micelles from the simplest *l*-ABC terpolymers in solutions. In fact, we will give more insight into the forming dynamics of these multicompartment micelles in the next work.

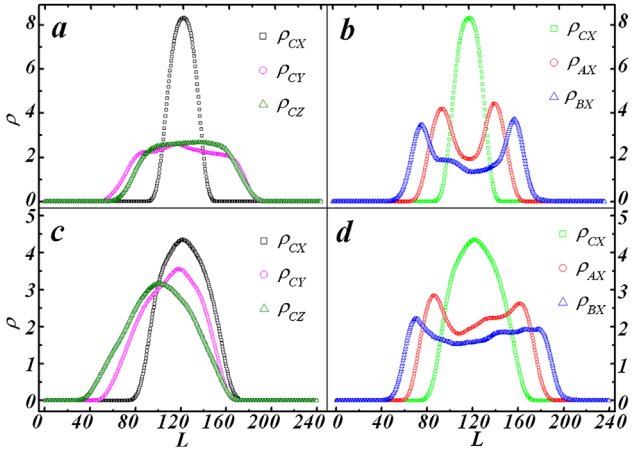

Figure 3. a) and c) the density profiles (ρ) in *x*, *y*, and *z* directions for the core of *l*-ABC (2-4-2) and (2-8-4), respectively; b) and d) ρ in *x* direction for the whole micelle of *l*-ABC (2-4-2) and (2-8-4), respectively.

Based on the morphologies in Figure 2, we give the phase diagrams of *l*-ABC terpolymers in the dilute solutions. The results are shown in Figure 4. The phase diagrams clearly provide a general understanding for the regions (or conditions) forming the particular multicompartment micelle. It must be firstly indicated that the mixed micelles (denoted by the mixed signals) hold the large area of phase diagrams, especially in Figure 4b–d. All the mixed structures are confirmed by the enough simulation time to avoid the nonequilibrium state of dynamics. For example, the novel raspberry-onion-like micelles can be formed only when *l*-ABCs have the longer weakly solvophobic B blocks ($B = 12$ or $y = 12$) and the shorter strongly solvophobic C blocks ($C = 2$ or $z = 2$). One of important conditions forming the bowl-like micelles is that *l*-ABCs, at least, have the longer solvophilic A blocks ($A \geq 8$ or $x \geq 8$). The cylinder and worm-like micelles mainly appear in the region of *l*-ABCs with the longer C blocks and B blocks. In conclusion, the shadows with the different color in the phase diagrams

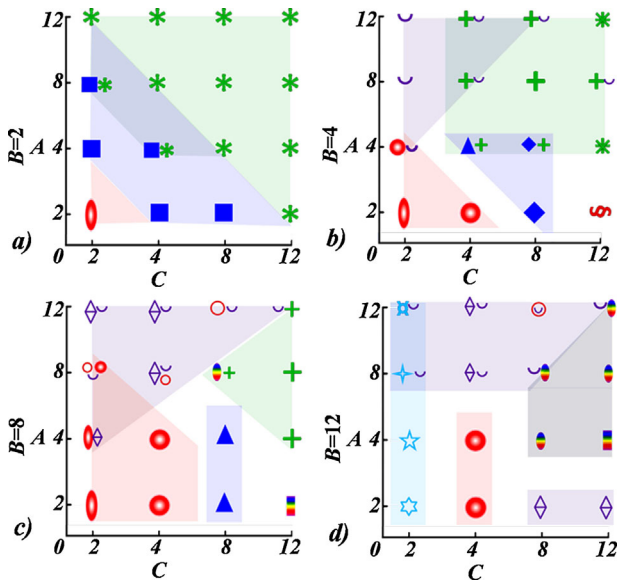

Figure 4. Phase diagram of *l*-ABC terpolymers in the dilute solutions. The same symbols with Figure 2 are used and the mixed symbols present the coexisted morphologies in one system.

clearly distinguish the formative areas of the different micelles. Of course, the overlapped parts indicate the emergence of mixed micelles.

4. Conclusion

We have investigated the self-assembly of the simplest *l*-ABC terpolymers in the dilute solutions using DPD technique. Besides the conventional micelles (core/shell/corona, raspberry, hamburger, etc.) predicted by the previous works, a number of new complex multicompartment micelles, such as raspberry-onion, cylinder and worm, cage, ring, helix-on-sphere, and so on, has also been predicted in our simulations. These micelle morphologies exceed the previous expectations for the self-assembly of *l*-ABC in solutions. At last, the detailed phase diagrams of *l*-ABC in solutions are provided, which clearly point out the conditions of forming the different micelles. Based on the phase diagram provided by our simulations, the experimental researchers can easily choose the complex multicompartment micelles, which have the special applications, from the simplest *l*-ABC terpolymers like μ-ABC star terpolymers.

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